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SUPERCONDUCTIVITY OF A15-PHASE Nb_3Si SYNTHESIZED BY Mbar SHOCK PRESSURE

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A15-phase Nb_3Si was synthesized by subjecting two 12 mm diameter and 1.5 mm thick discs of Nb_3Si in the majority phase of Ti_3P to Mbar shock pressures and quench rates up to 10^9 K/s and 10^{12} bar/s. Shock waves were generated by the LLNL two-stage light-gas gun. X-ray data indicate that a substantial portion of the A15 cubic phase was synthesized at the expense of the tetragonal phase of the starting specimen. The ocurrence of superconductivity in these specimens was determined by measurements of electrical resistivity and ac magnetic susceptibility, χ_{ac}, onsets of superconductivity are 17.8 K.

1. INTRODUCTION

Metastable materials offer a greatly expanded number of novel structures with interesting physical properties relative to materials synthesized with equilibrium techniques. In the area of superconductivity, for example, all A15 phases with superconducting transition temperatures $T_c > 18.5$ K are metastable.[1] Nb_3Ge is the A15 compound with the highest[2] T_c (23 K). This specimen was a film, synthesized by covapor deposition. Stoichiometric A15 phase Nb_3Si was predicted to have T_c in the range 25-38 K[3-6] and has been synthesized with T_c = 18 K only by subjecting specimens to Mbar (10^6 bar) shock pressures.[7-11] New, stable Y-Ba-Cu-O compounds have been synthesized with T_c above 90 K. However, what are now thought by some to be short-lived metastable phases displaying signals indicative of superconductivity have been observed[12] up to 148 K. This suggests that the highest critical temperatures in the new oxides might also be obtained in metastable phases, as for the A15's.

In order to synthesize metastable materials we have developed a technique to subject specimens to dynamic pressures of up to the Mbar range and dynamic temperatures up to a few 1000 K. The high pressures induce densities up to ~30% higher than the initial solid density, thus accessing a new plane in the phase diagram. The quench rates are up to 10^{12} bar/s and 10^9 K/s. The pressure quench rate is the maximum possible. The thermal quench rate is the largest possible in macroscopic specimens. Nb_3Si was chosen as a test material because the stoichiometric A15 compound is known to be synthesized by very high dynamic pressure.[7-11] However, specimens had not yet been reported with a complete resistive transition to the superconducting state, indicating that improvements to the dynamic synthesis technique were possible.

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2. SYNTHESIS BY HIGH DYNAMIC PRESSURE

The method is similar to that used previously at Tohoku University with a two-stage light-gas gun.[10,11] Our experimental configuration is illustrated in Fig.1 and utilizes the LLNL two-stage gun. Dynamic extreme conditions are generated by the impact of a Cu-plastic projectile onto a Cu capsule which contains the specimen. The Cu capsule is contained in a Pb-steel fixture; this fixture is discussed elsewhere.[13] The recovery fixture is precooled to liquid nitrogen temperatures in order to maximize the quench rate and minimize the residual shock temperature.

The impactor velocity U_I (measured by flash x-radiography[14]) and the known equation of state of Cu yield the impact pressure by the shock impedance matching technique.[15] Breifly, shock pressure on impact is given by the Rankine-Hugoniot relation,

$$P = \rho_0 U_s U_p \qquad (1)$$

where ρ_0 is the initial specimen density, U_s is the shock

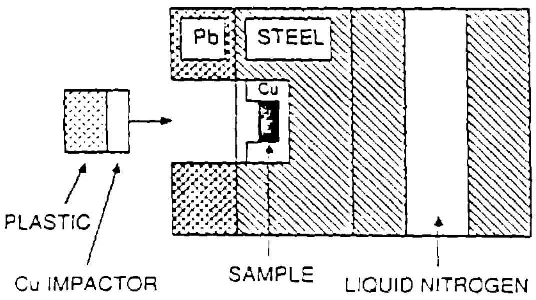

FIGURE 1
Cross sectional schematic of cylindrical fixture for subjecting disc specimens to Mbar shock pressure and recovering them intact after rapid quenching.

velocity generated by the impact, and U_p is the mass velocity behind the shock front. For Cu

$$U_s = C + SU_p \qquad (2)$$

with[16] C = 0.3933km/s and S = 1.500. For a symmetric impact like Cu on Cu, $U_p = U_i/2$.

The advantage of this technique is that an impactor weighing less than 10 g interacts with the fixture. The driving gases of the gun are decoupled from the impactor when it enters the evacuated target chamber. The small impactor minimizes the momentum and kinetic energy that must be dissipated, causing the high dynamic pressures and temperatures to be localized in the immediate vicinity of the specimen. This allows the steel backing material remain to intact and also act as a massive low temperature heat sink for quenching since it is essentially unheated by the shock wave. Energy considerations for this technique will be discussed elsewhere.[13]

3. MATERIAL PREPARATION

Samples were prepared by arc-melting the proper stoichiometric amounts of 99.99% Nb and 99.999999% Si together on a water-cooled Cu hearth under an atmosphere of argon. The resulting arc-melted ingots were then spark erosion cut into the shape of discs 12 mm in diameter and 1.5 mm in thickness. These discs were annealed at 1800 K for 60 hours in a vacuum in order to promote the majority phase of Ti_3P tetragonal structure. X-ray analysis of these samples indicated the majority phase was Ti_3P with some Nb_5Si_3 and Nb impurity phases.[17] The annealed discs were enclosed in the Cu capsules mentioned above. These capsules were specially machined to the size of each disc within 20 mm. The loaded capsules were placed in the Pb-steel fixture with the sample centered on the axis of the launch tube of the gun near the muzzle. Two samples were subjected to dynamic pressures with respective peak pressures of 0.82 and 0.96 Mbar. These pressures were generated with impactor velocities of 2.99 and 3.33 km/s respectively.

4. RESULTS AND DISCUSSION

Following the shock treatment the Cu capsules were completely etched away from the Nb_3Si discs with nitric acid, the uncovered discs were still intact. When touched, the 0.82 Mbar specimen broke apart into chunks and powder. In contrast, the 0.96 Mbar specimen was much more robust. While it did possess many cracks, it required reasonable effort to break into pieces for further study. These properties indicate that the higher shock pressure generated more heating which increased ductility and helped keep the sample together.

X-ray analysis of these specimens indicate that some interesting structural transformations have taken place as depicted in Fig. 2. The change in intensity of the x-ray peaks relative to the Nb (110) impurity peak indicates that the Ti_3P phase Bragg peaks decrease in intensity as shock pressure is increased while two new peaks rise from the spectrum: these peaks become better defined with increasing shock pressure. We compared the two peaks with a computer generated x-ray diffraction pattern

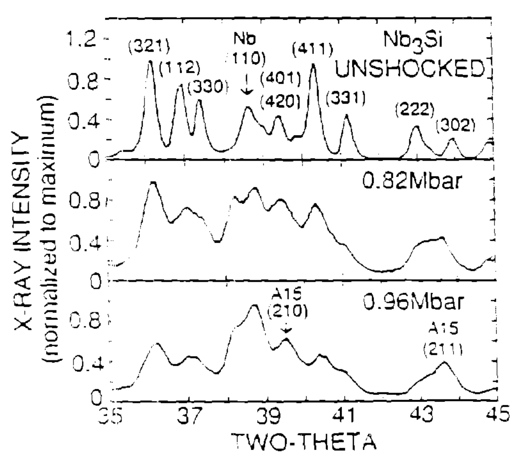

FIGURE 2
Normalized x-ray intensity vs. two-theta angle for shocked and unshocked Nb_3Si specimens. Peaks are labeled with Miller indices which unless otherwise indicated refer to Ti_3P

calculated with the program LAZY-PULVERIX;[18] they appear to belong to the (210) and (211) reflections of A15 Nb_3Si with a lattice parameter of 5.09 ±0.01 Å in agreement with the results of reference 7. These peaks are rather broad, which is an indication of disorder. The A15 phase remained stable after annealing the 0.96 Mbar specimen at 500°C for 5 days. Annealing at other temperatures is being carried out and will be discussed elsewhere.[13]

Resistivity measurements were carried out on irregularly shaped pieces (~3x1.5x1.5 mm^3) broken off of the shock treated discs. Platinum leads, spot-welded to the specimens, provided contacts for the four-lead, 16 Hz ac measurements. Resistivity data are shown in Fig. 3 for temperatures below 30 K; above 30 K all specimens exhibited metallic type resistive behavior. The unshocked specimen (not shown) enters the superconducting state with T_c = 8.7 K (T_c is defined as the temperature where the resistivity drops to 50% of the normal state value). The Ti_3P phase of Nb_3Si should become superconducting with[19] T_c= 0.29 K; the transition at 8.7 K is probably due to some Nb-Si impurity in our specimens. The two 0.82 Mbar specimen transitions plotted exhibit well defined drops in their resistivities starting at ~18 K. These drops then leve off until the specimen appears totally superconducting at the Nb-Si transition. The behavior of these transitions illustrate the multiphase nature of the 0.82 Mbar specimen, displaying its lack of a complete high temperature superconducting path. In contrast, the 0.96 Mbar specimen has a complete, resistive, high-temperature, transition to the superconducting state. The resistivity of two samples broken off of the same 0.96 Mbar disc are shown in Fig. 3. One of these samples (shown in the lower curve) exhibits 10% and 90% drops in the resistivity from the normal state value at 17.6 and 17.3 K respectively, the difference of these two values is defined as ΔT_c. The resistance became too small to detect (<1 μΩ, we refer to this as "zero resistance") by 17.2 K. The other transition shown in the figure has ΔT_c = 0.85 K but the resistance does not drop to zero until 13 K.

Resistivity measurements indicating superductivity can at times be misleading. Superconducting paths comprised of tiny filaments made up of minority phases (possibly located along grain boundaries) can create signals indicating zero resistance when in fact under 1% of the sample is actually superconducting. In order to clarify this point, we measured the response of these specimens to an inductive ac signal (20 Hz) in bulk and powdered forms. The powdering is carried out as a means of breaking up any superconducting filaments that might exist in the sample. These data are shown in Fig. 4. The 0.82 Mbar sample has a very small transition that begins at 17.7 K and extends down to the Nb-Si transition. Powdering has very little effect on this transition. The 0.96 Mbar specimen has a much larger transition which begins at the same temperature as the 0.82 Mbar specimen. Powdering in this case lowers the transition in temperature slightly (<0.2 K) but does not modify it significantly.

In conclusion, shock pressures of 0.82 and 0.96 Mbar have induced the superconducting A15 phase of Nb_3Si. Resistivity, inductive measurements, and x-ray data indicate the multiphase nature of these specimens with the largest amount of A15 phase produced in the 0.96 Mbar

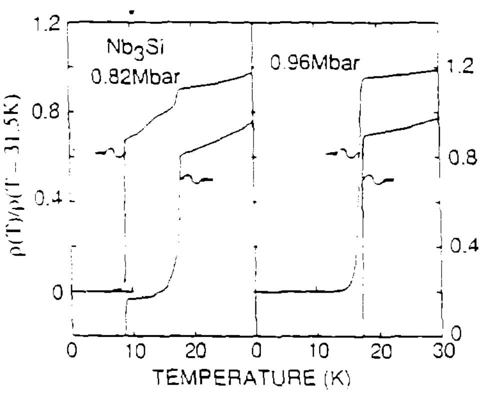

FIGURE 3
Normalized resistivity vs. temperature for shock treated specimens; arrows indicate appropriate scales.

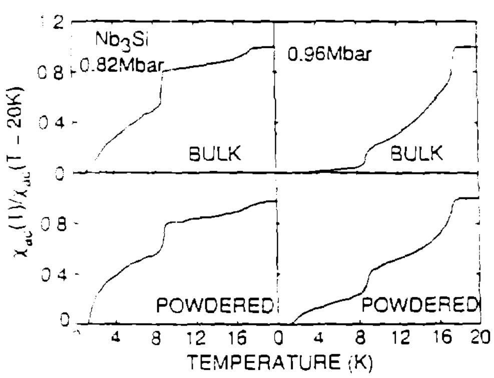

FIGURE 4
Normalized ac magnetic susceptibility ,χ_{ac},vs. temperature for bulk and powdered shock treated specimens.

specimen. Further studies on these specimens have been carried out, including metallography, upper critical field, specific heat, and the effect of hydrostatic pressure on T_c. These results will be reported elsewhere.[13]

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